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CHEMICAL VAPOR DEPOSITION STUDY

Semi-annual Progress Report

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I. INTRODUCTION

The research activities of the Division of Materials Science and Engineering into chemical vapor deposition, supported by the Advanced Research Projects Agency, are now 1-1/2 years old. Barring unforeseen difficulties, we have now largely progressed from the planning stages, through the equipment stages, to the data acquisition stages. This rate of progress is as originally projected or better.

The reports given in the subsequent technical section document progress in the several areas of investigation.

II. TECHNICAL REPORTS

A. Mechanical Behavior

The tensile properties of C.V.D. tungsten in the as-received condition were measured at a strain rate of $0.02/min^{-1}$ from 800°C to 1400°C in a helium gas atmosphere.

1. Preparation of C.V.D. tungsten specimens for tensile test

Gage lengths for flat tensile specimens were cut in a Servomet Spark Machine, Model 80-901. The cutting tool used in this work was a piece of 0.020" thick copper sheet. The spark erosion speed was set on range 5 for a few minutes and then set on range 4 to complete the cut. The time to complete a cut 0.040" thick flat specimen is approximately 4-5 hours. 1/8" diameter holes were formed near each end in order to pin the specimen to the extension rods.

The tool used to make the 1/8" diameter holes was a 1/8" diameter 2% thoriated tungsten alloy. The time to make a 1/8" diameter hole is approximately 2-3 hours. Any slight damage to the specimen caused by spark cutting was removed by electropolishing. (20 gr NaOH + 980 cc distilled water.) The electropolishing process produced a reduction of thickness of approximately 0.002". The final dimensions of the specimens were 0.038 inch thickness, 0.125 irch width and a gage length of 0.5 inch. The over-all specimen length was 2.25 inches. A typical tensile specimen is illustrated in Figure 1.

2. Temperature Measurements

Temperature measurements were made with an optical pyrometer calibrated by the National Bureau of Standards. The observations were made,

through a 1/8" hole in the tantalum susceptor which was a 1" diameter tantalum tube. In addition, a tungsten-5% rhenium--tungsten-26% rhenium thermocouple was placed near the specimen. Under conditions of thermal equilibrium at 1900°C a maximum temperature difference of 40°C was detected between the thermocouple and the optical pyrometer. The results are shown in Figure 2.

In all the tensile tests the temperature was measured by optical pyrometry.

3. Testing Procedure

With the load train and specimen installed, the chamber was evacuated by a mechanical pump. Then pure helium gas was delivered to the chamber. The specimen was then slowly heated to the test temperature. Tensile tests were performed with a floor model Instron Tensile Machine. The temperature dependence of yield and ultimate tensile strength were determined.

4. Results

The yield stress and tensile stress results are summarized in Table 1. Figure 3 shows the results in terms of the 0.2% offset yield stress and ultimate tensile stress is a function of the test temperature. Figure 4 shows the elongation (%) as a function of the test temperature.

Ultimate tensile strength at 1000°C and 1200°C are 14,000 psi and 12,000 psi, respectively. These values are in good agreement with Taylor's[1] result. The elongations of 24 to 30% from 800°C to 1400°C are also in good agreement with Taylor's results. These data will be utilized to calibrate the hoop stress testing apparatus.

TABLE 1. TENSILE TEST DATA

Temperature	Y.S.(psi)	T.S.	Elongation %	Atmosphere
800°C	9,600	19,000	24	He Gas
1000°C	8,500	14,000	26	Argon gas
1200°C	7,300	12,000	26	He gas
1400°C	6,600	?	30	He gas

B. Annealing Studies

Grain growth studies have been completed for isothermal anneals of up to thirty hours at fourteen temperatures between 1290°C and 2780°C for a tungsten-22 wt. % rhenium alloy. Figures 5 and 6 are linear plots of $D^2-D_o^2$ versus annealing time. Of particular interest are the negative values for the 1290°C curve in Figure 5. In the annual progress report (September 1969) and in the Second International Conference on C.V.D. some similar findings were reported for pure tungsten for which plots of log $(D^2-D_o^2)$ versus log time for isothermal anneals at 1290°C, 1405°C, and 1520°C showed negative slopes. The latter negative slopes were thought to indicate a nucleation process, however, later considerations led us to reinterpret these data as indicating simply that at these lowest annealing temperature certain small grains, which were submicroscopic in the as-received condition (and hence not averaged in), became measurable at the lowest temperature anneals, and decreased the average grain size. For subsequent higher temperature anneals the average grain size simply increases. Some of the reasons behind this reinterpretation were:

1) X-ray studies of line broadening indicated an absence of

appreciable microstrains in the as-received material which, in turn, precluded the existence of much stored energy of 'cold work' to provide a driving force for conventional recrystallization,

2) the "nuclei" were not found in the midst of a distorted matrix but rather among rather equiaxed grains,

3) had conventional recrystallization started at these lower temperatures, the columnar microstructure would not have persisted which, in fact, it did.

In the 5th Quarterly Management Report it was stated that these negative slope measurements would be repeated so as to assure validity. This has been done and the previous results were valid.

As was the case for the above described tungsten results, the tungsten-22 wt. % rhenium alloy in showing negative deviations of $D^2-D_o^2$ versus time at 1290°C (Figure 6) is probably not recrystallizing but merely undergoing ordinary grain growth. The recrystallization possibility, although remote, will be checked by some X-ray line broadening experiments. The possibility is kept open because the negative deviations of $D^2-D_o^2$ versus time in the alloy data mean that the D is actually smaller than the as-received D_o, whereas a negative slope of log $(D^2-D_o^2)$ vs. log time (pure tungsten) meant only that grains were appearing which were smaller than the average size at the annealing temperature but not smaller than the as-received size since negative values are impossible on the log-log plot. A second reason is that there appear to be deformation twins in the microstructure of the alloy (replicas will be made to check this more certainly) which could provide good recrystallization nuclei.

In Figure 5 notice is called to the difference between the curves E1800 and R1800 (both for 1980°C). The former curve is based on thermal grooving measurements; the latter is based on subsequent electropolishing and etching. The difference reveals the effect of surface restriction of grain growth relative to grain growth in more interior regions.

If one compares Figure 5 with Figure 7, which is for pure tungsten, it is seen, for example, that 30 hours at 1750°C produces a grain size change in the alloy of approximately twice that of the pure tungsten. This at first seems strange, but it may be caused by the fact that the tungsten data were obtained by observing the end view of columnar grains whereas the alloy data were obtained from the growth of equiaxed grains. It is, perhaps, of importance to note this two-fold difference of growth rate in connection with grain morphology. This point will be pursued in our future work.

Figure 8 shows the experimental data used to obtain the activation energy for grain growth of the alloy. A value of 61.7 kcal/g-at was obtained. This is reasonable compared to the value obtained earlier for tungsten--59 kcal/g-at (to be presented at 2nd International Conference on C.V.D., May 12, 1970).

It is interesting to note certain microstructural features of the alloy. Figure 9 shows the as-received condition. Note a number of square grains, as well as a suggestion of growth steps. Figures 10a and 10b furnish clearer evidence of the existence of growth steps. Finally, it is interesting to compare Figure 11, which represents a 60 hour anneal at 1290°C (where negative $D^2-D_o^2$ values existed), with Figure 9, the as-received condition. It is seen that, indeed, the grain size is less than that of the as-received material as was discussed earlier.

C. Residual Stress

Efforts to accurately calibrate residual stress determinations using a split ring of tungsten with an internal strain gage are continuing. One problem has been the rough surface of the tungsten which contains projections that do not represent the true surface stress but which do, unfortunately, contribute strongly to the diffracted intensity. Some electropolishing will be introduced to improve surface finish but, hopefully, not enough to release any significant stress. Continual realignment of both diffractometer and stress track have reduced the expected maximum error to $\pm$ 2100 psi.

Residual stresses in a tungsten tube deposited at the University of Utah on the interior of a copper tube have been studied (see below). When the copper was etched away, fractures caused the thin (.003") tubing to curl in on itself from an initial diameter of 1-1/2" to approximately 1" or less. A rough calculation of the residual stress[2] was made using:

$$\sigma_c = \frac{E}{1-\nu^2} t\left(\frac{1}{D_o} - \frac{1}{D_f}\right)$$

where t = thickness in inches

σ_c = circumferential stress

ν = Poisson's ratio = 0.27

E = Young's modulus = 58×10^6 psi

D_o = initial diameter in inches

D_f = final diameter in inches

The result is a compressive stress of 62,600 psi in the surface which had been next to the copper substrate surface. It would seem that in the

fine-grained side of the material a more severe competition between the smaller, first nucleated grains results in a compressive residual stress of considerable magnitude. This will be checked further.

Pinhole X-ray photos will be taken on both sides of one of these highly curled pieces to see if any A15 unstable phase is present (a_o = 5.05Å). The normal tungsten a_o is 3.165Å. Some A15 phase on the substrate side could, perhaps, account for the curvature found.

D. Texture Study

An inverse pole figure was determined for a flat piece of C.V.D tungsten supplied by Fansteel Metallurgical. This type of material was used in the tensile tests reported above. Table 2 summarizes the averaged Texture Coefficients (T.C.) found:

TABLE 2. AVERAGED TEXTURE COEFFICIENTS

Direction	Average T.C.
<100>	1.35
<310>	1.15
<110>	1.0
<211>	0.9
<123>	0.6

Thus, in looking at the flat surface, one sees mostly a cube direction texture. This is less pronounced, however, than the basic cube textures found in looking at the o.d. of Fansteel tubes (Semi-annual Progress Report). Further work here is advisable. In particular, the substrate

and outer surfaces of flat material used for tensile testing should be checked for textural differences.

E. Material Production

The production facility is now operational and it is possible to make pure tungsten tubes having a thickness of 30 to 40 mils over a length of about 4". From such tubes, ring specimens are to be cut for hoop stress measurements. Several problems have been solved in this work. One of these concerns the trapping of the product gas HF. In the original trapping system liquid nitrogen alone was used. These traps would fill up rapidly and sometimes runs had to be cut short due to the increased resistance to flow and consequent difficulty in holding the system pressure at a prescribed level. We have subsequently inserted a chemical trap into the line between the scavenger furnace and liquid nitrogen trap. This chemical trap consists of pellets of NaF which react with the product gas HF to form $NaHF_2$. The NaF may be regenerated at the operator's convenience by holding the $NaHF_2$ at 300°C for a period of about one hour. This has proved to be a much better way to handle the product gas HF.

We have checked other workers[3] in determining optimum conditions for deposition in our production facility. These conditions are as follows: temperature 550°C, pressure 300 torr, WF_6 flow rate 220 cc/min, and H_2 flow rate 2000 cc/min. Our microstructure is typical of what has been reported for pure (unbrushed) tungsten. Fine grains begin at the copper substrate but give way to coarse columnar grains within about one to two mils from the substrate.

Our tubes appear to contain considerable internal stresses in the as-deposited condition. This became apparent when it was observed that a tube 5 mils in thickness curled in (away from the substrate) when cut

parallel to its axis. These stresses may not be directly related to the substrate material or its geometry, since we have noticed similar phenomena for deposits on flat metal strips of iron, copper, and nickel. They may be directly related to the change in microstructure occurring near the substrate. This matter is discussed elsewhere in the report.

F. Deposition Kinetics

Kinetic studies are underway. At present we are determining what flow rates, temperatures, and pressures will insure deposition in the surface-controlled regime. An interesting observation in this early work is that the kinetics of the first few mils of deposition may be noticeably different from the kinetics observed during the remainder of the deposition. If this is so, then we may be able to correlate microstructure and kinetics.

G. Alloy Program

Our alloy program is still in the planning stages. Since the main goal of this program is to improve the microstructure of C.V.D. tungsten by refining the grain size, we are considering non-mechanical ways of inhibiting grain growth and promoting nucleation. It has been observed[4] that tungsten, produced using a tungsten hexachloride feed, has a somewhat better microstructure and that the columnar grains have a different orientation then for the tungsten hexafluoride feed. Because of this fact, it seems worthwhile to perform several experiments in which small amounts of chlorine or chlorides are introduced into the system. It is contemplated that the chloride may be introduced as a hydrogen, vanadium, or molybdenum chloride.

REFERENCES

1. J. L. Taylor and D. H. Boone, J. of the Less-Common Metals, 6, 157, (1964).

2. G. Dieter, Mechanical Metallurgy, New York: McGraw-Hill, 1961, p. 407.

3. W. R. Holman and F. J. Huegel, Proc. Conf. C.V.D., Gatlinburg, Tennessee, p. 19 (1967).

4. Private communication, Fred A. Glaski, Fansteel, Inc., San Fernando Laboratories, 10258 Norris Ave., Pacoima, California.

LIST OF FIGURES

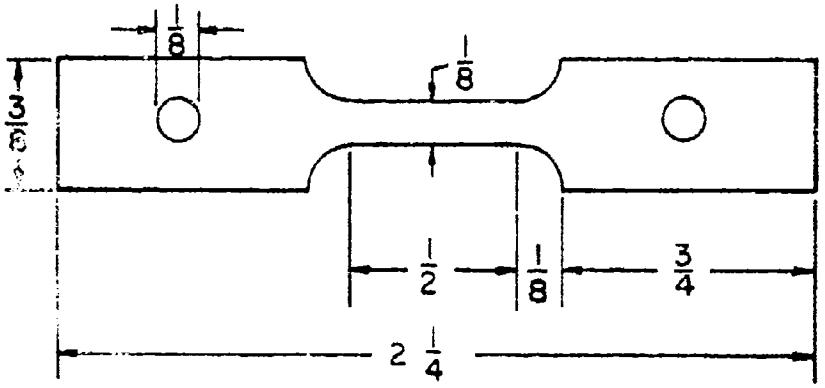
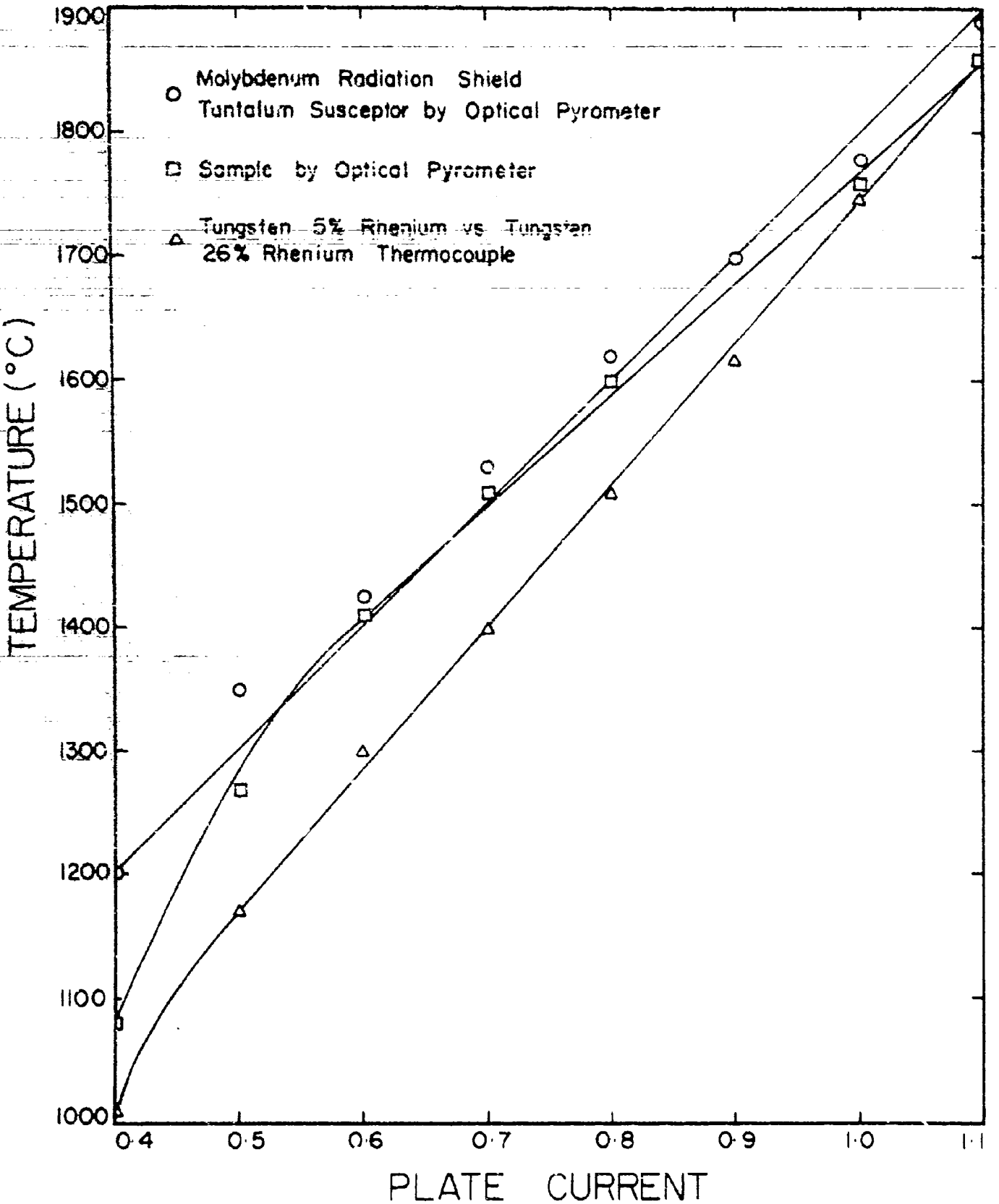
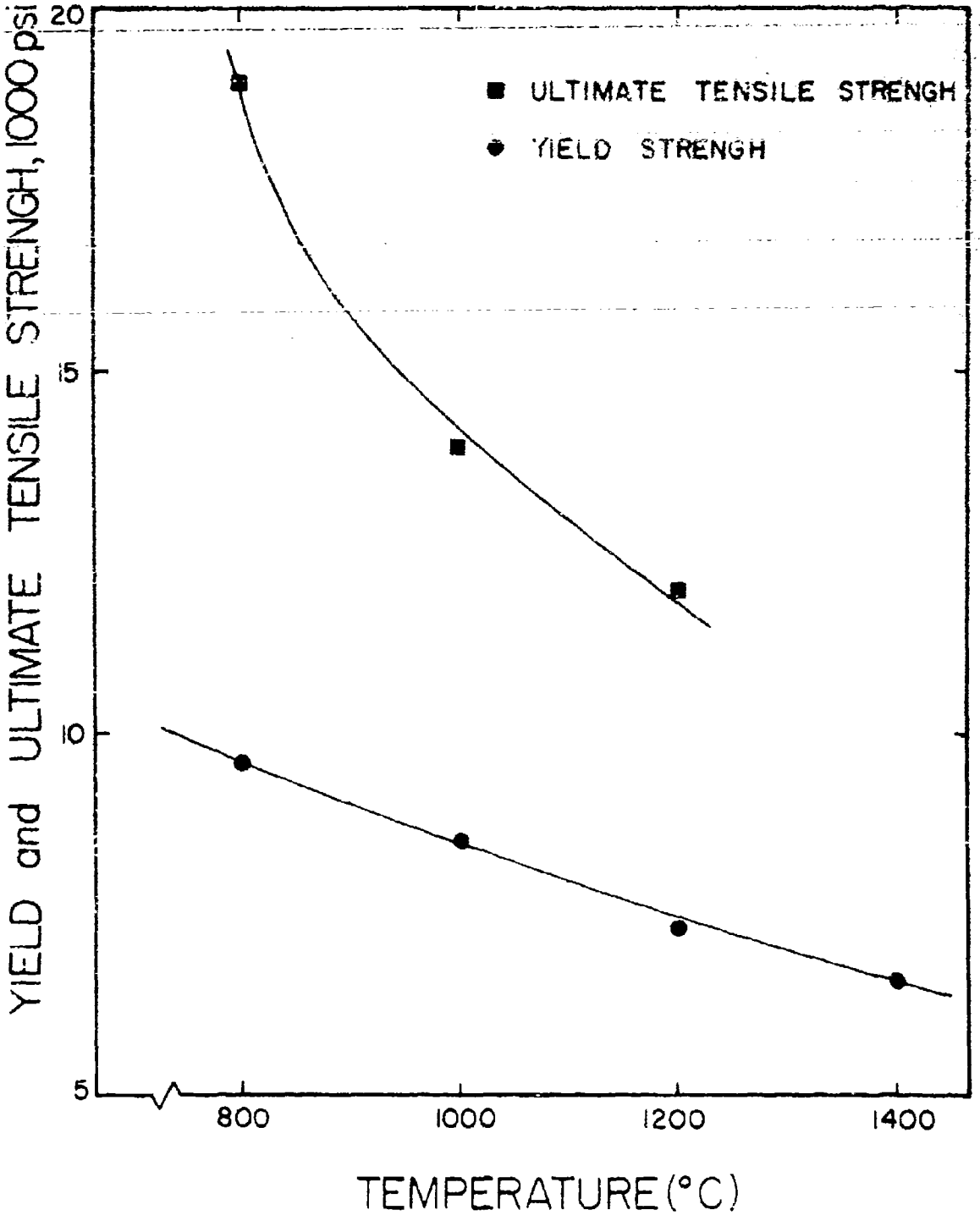
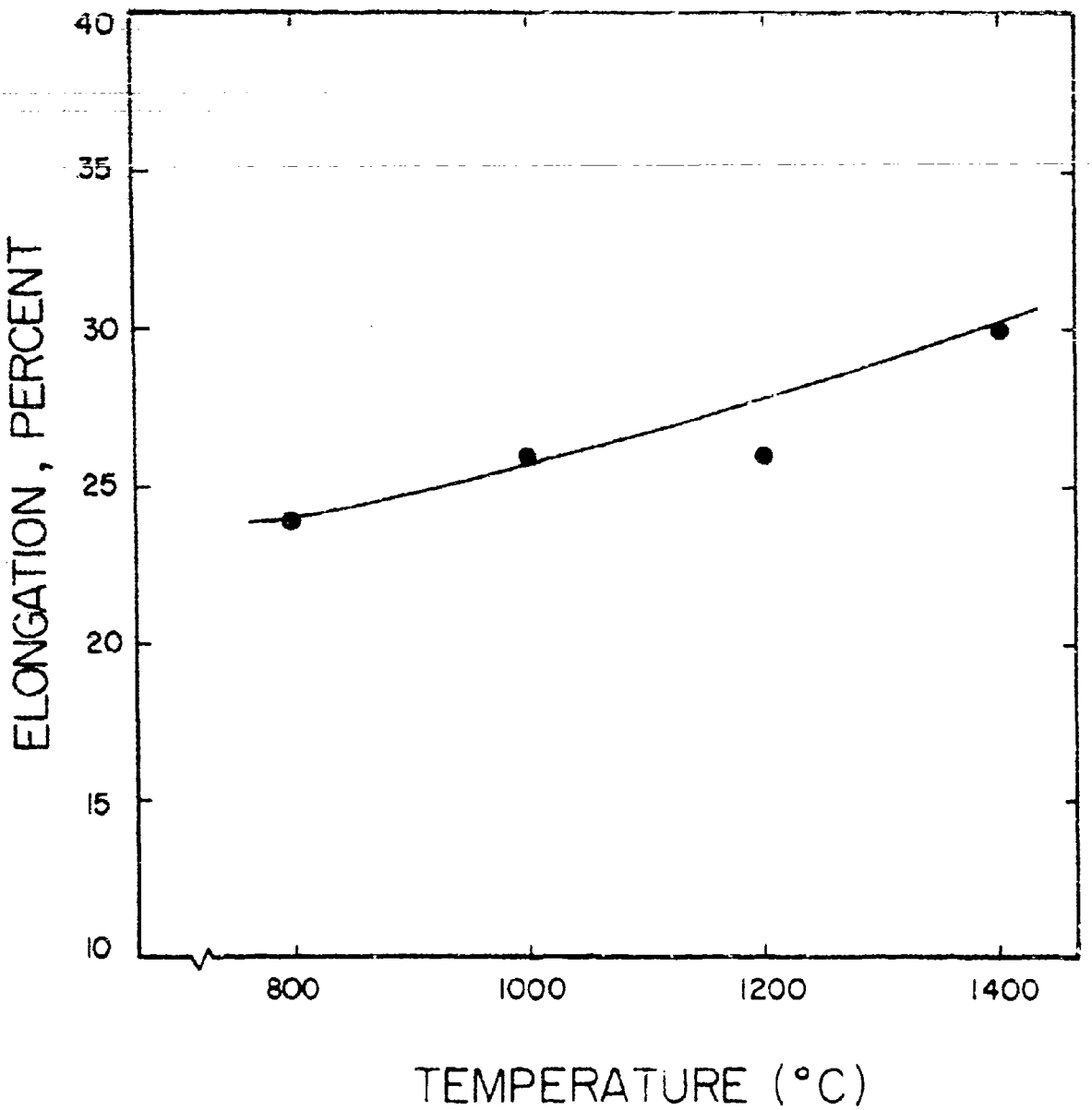
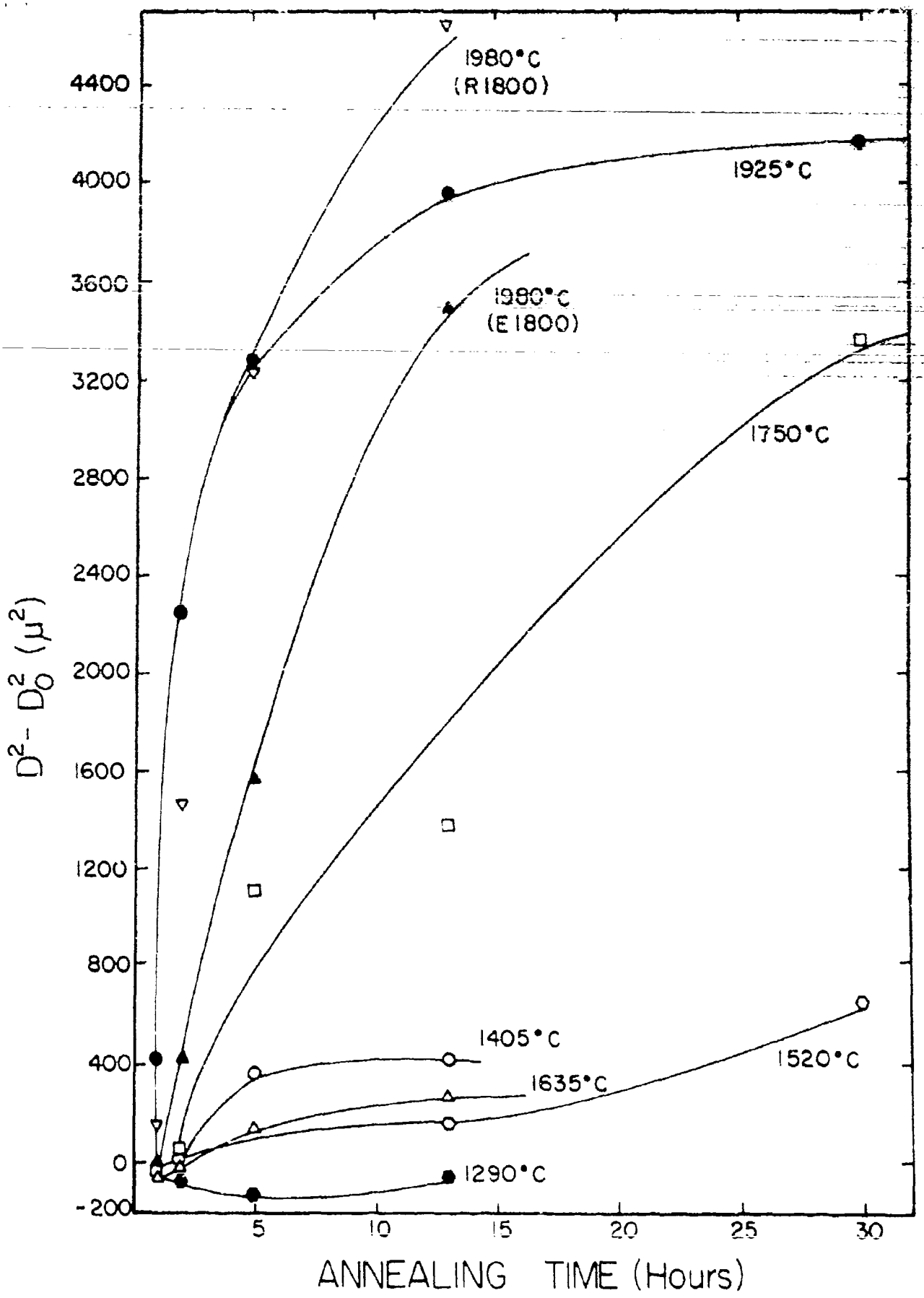


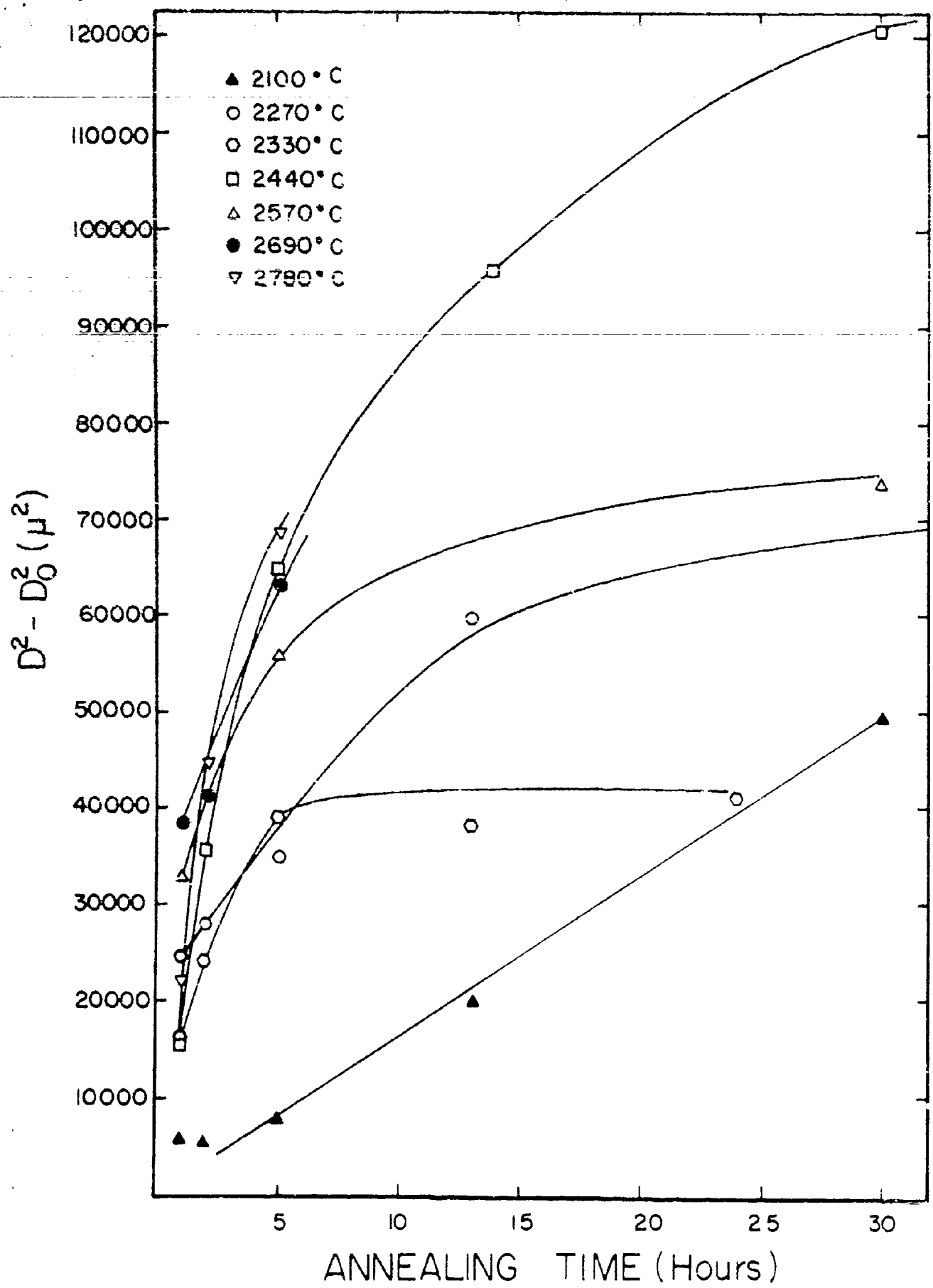
DIAGRAM OF TENSILE SPECIMEN

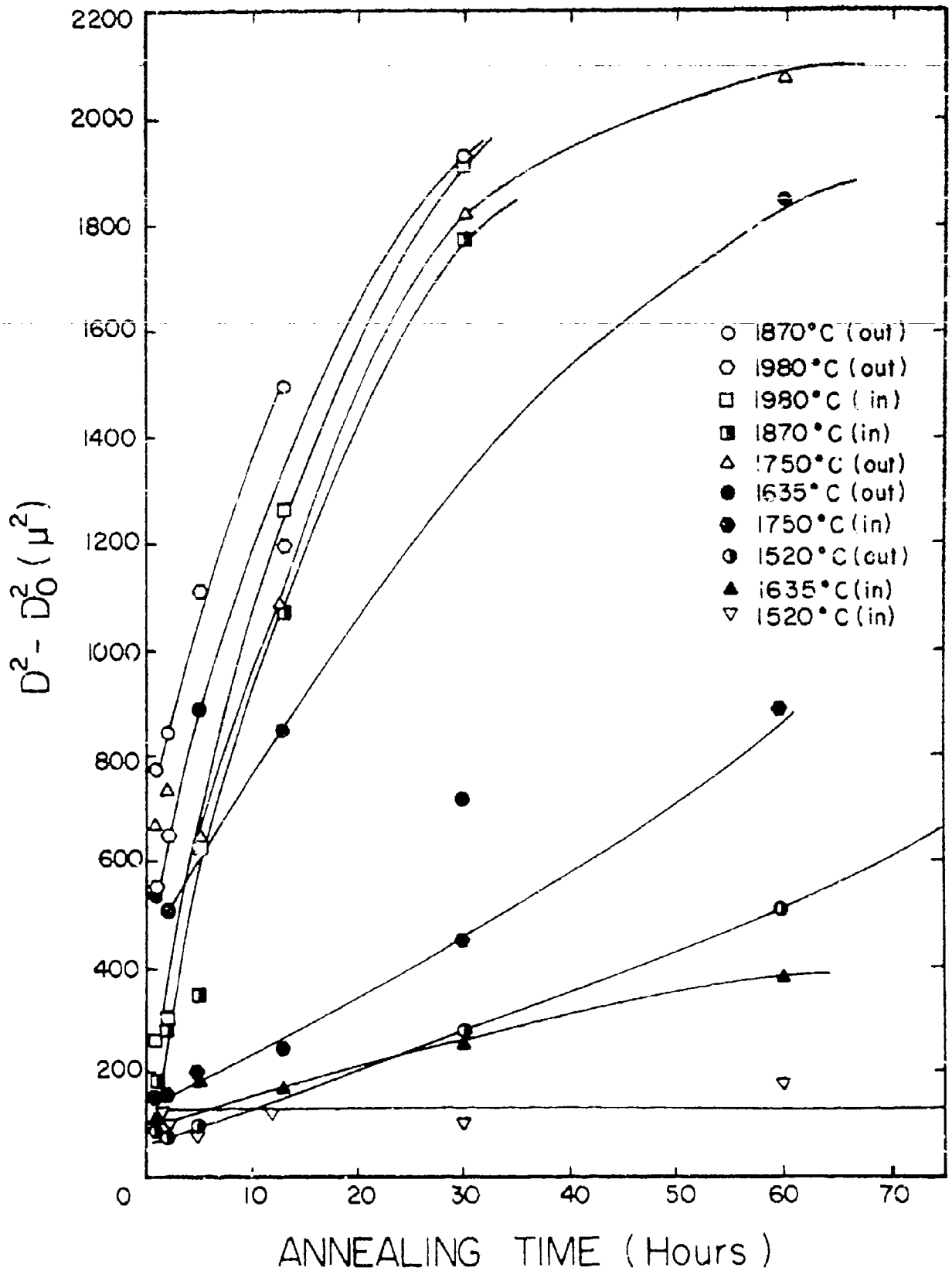

Molybdenum Radiation Shield
Tantalum Susceptor by Optical Pyrometer
Sample by Optical Pyrometer
Tungsten 5% Rhenium vs Tungsten
26% Rhenium Thermocouple
TEMPERATURE (°C)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
PLATE CURRENT

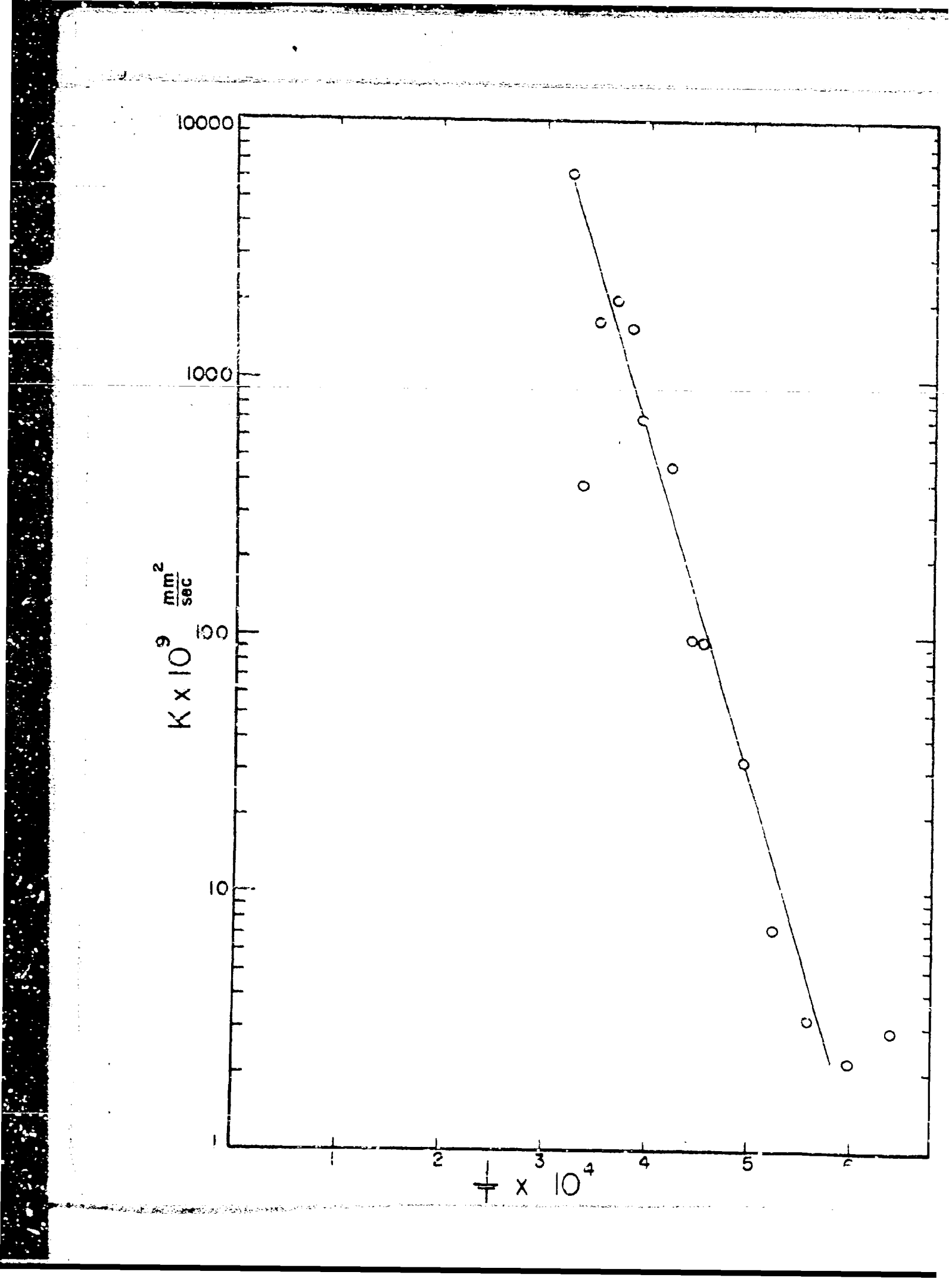

YIELD and ULTIMATE TENSILE STRENGH, 1000 psi
20
15
10
5
ULTIMATE TENSILE STRENGH
YIELD STRENGH
800
1000
1200
1400
TEMPERATURE (°C)


40
35
30
25
20
15
10
ELONGATION, PERCENT
800
1000
1200
1400
TEMPERATURE (°C)


1980°C
(R1800)
1925°C
1980°C
(E1800)
1750°C
1405°C
1635°C
1520°C
1290°C
4400
4000
3600
3200
2800
2400
2000
1600
1200
800
400
0
-200
5
10
15
20
25
30
D² - D₀² (μ²)
ANNEALING TIME (Hours)


▲ 2100 °C
○ 2270 °C
○ 2330 °C
□ 2440 °C
△ 2570 °C
● 2690 °C
▽ 2780 °C
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
$D^2 - D_0^2 (\mu^2)$
5
10
15
20
25
30
ANNEALING TIME (Hours)


2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
10
20
30
40
50
60
70
$D^2 - D_0^2 (\mu^2)$
ANNEALING TIME (Hours)
1870°C (out)
1980°C (out)
1980°C (in)
1870°C (in)
1750°C (out)
1635°C (out)
1750°C (in)
1520°C (out)
1635°C (in)
1520°C (in)


10000
1000
100
10
1
K x 10^9 mm^2/sec
1
2
3
4
5
6
1/T x 10^4